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Microwave dielectric relaxation and molecular dynamics in ternary mixtures of poly (vinyl pyrrolidone) -poly (propylene glycol) -poly (ethylene glycol)s of varying molecular weights in non-polar solvent

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Abstract . Molecular dynamics of ternary mixtrues of poly (vinyl pyrrolidone) (PVP) (Mw = 40000 g mol^{-1}), poly(propylene glycol) (PPG) (Mw = 2000 g mol^{-1}) and poly (ethylene glycol)s (PEGs) (Mw = 200, 400 and 600 g mol^{-1}) with PVP concentration variation has been explored in dilute solutions of benzene using microwave dielectric relaxation times at 10.1 GHz and 35°C. The average relaxation time τ_0, distribution parameter α, relaxation time corresponding to segmental motion τ_1 and group rotations τ_2 has been determined for the PVP-PEGs-PPG mixtures in benzene solvent. The large value of $\alpha \approx 0.3$ to 0.63 of these polymers and their mixtures confirms that besides the overall rotation there is large contribution of the segmental motion and group rotations in dielectric relaxation processes. The dynamics of PEGs molecules has been explored by considering the chain coiling and intra- and intermolecular hydrogen bonding in the complex heterogeneous species with the help of observed values of relaxation times. It is found that the values of τ_0 and τ_1 are independent of the mixture viscosity. The observed values of τ_2 are attributed to the rotation of chain ends hydroxyl groups/ methyl side-groups of these polymer molecules. The free energy of activation ΔF_r of these systems has also been evaluated. These values are found in the range of ≈2–4 kcal mol^{-1}.

Keywords PVP-PEG-PPG mixtures; dielectric relaxation times, molecular dynamics

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1. Introduction

The polymers PVP, PEG and PPG have wide applications as chemical intermediates, pharmaceutical aids, anti-foaming agents in fermentation, paint formulations, binders and lubricants for ceramics, plasticizers *etc* [1-3]. For their significant applications, it is important to understand in detail, the structural dynamics of these polymers in various environments. These macromolecules form intra- and intermolecular hydrogen bonding because of several hydrogen bonding sites present in molecular chain, that give rise to different conformations. Consequently, these macromolecules are known to self-associate and also to associate with polar solvents of other polymers. The mixing of polymers may result in the formation of inter-polymer complexes due to hydrogen bonding, and hence these mixtures may possesses the qualitatively new properties for different applications. Any attempt to characterize the motion of a macromolecular mixture in terms of a coordinate system located at each atom becomes an almost impossible task. Therefore, several attempts have been made to study the dynamics of these molecules using a variety of relaxation, absorption, fluorescence and scattering techniques. For investigating the molecular dynamics of oligomers and polymer molecules, microwave dielectric relaxation studies [4-8] has proved as a powerful tool. These studies are used in understanding the flexibility of the molecular chain, mobility of the polymer segments, internal group rotations, steric hindrance to the internal rotations due to hydrogen bonding and solvent effect on these rotations of the associating molecules in non-polar solvents.

The miscibility of high molecular weight PVP with short chain PEGs has been shown to be the result of hydrogen bonding of the PEG terminal hydroxyls to the carbonyls in the repeating

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units of comparatively longer PVP macromolecules [9-10]. Since both H-donor hydroxyls at the ends of short chain PEGs are involved into cross links H-bonding with high degree of orientation with respect to longer PVP chain assembling the longer PVP macromolecules into an ordered specific super molecular structure. Such structure have enhanced free volume and large molecular mobility [11] with rubber like elasticity [9] and unique physical properties such as pressure-sensitive adhesion [12], featured only for PVP-PEG complex of stoichiometric composition but not for parent polymers [13]. The molecular dynamics and stoichiometry of the PVP-PEG network complex have been extensively studied by Feldstein *et al* using Fourier Transform Infra Red (FTIR) spectroscopy [9], Differential Scanning Calorimetry (DSC) [14-19] and rheological methods [9,20-22] for the development of universal transdermal drug delivery systems (TDDS).

Earlier in this laboratory [4-6,23-26], several attempts were made to explore the molecular dynamics of PEGs and PPG2000 in dilute solutions of non-polar solvent and also in pure liquid state with polar solvents. Microwave dielectric relaxation studies of binary mixture of PPG2000-PEGs and PVP-PEG200 in dilute solutions of benzene were carried out to confirm the heterogeneous molecular interactions, chain coiling, intra molecular rotations and elongation of the complex heterogeneous network of these polymers in non-polar solvent. In the extension of the earlier studies, in the present investigation, an attempt has been made to explore the molecular dynamics and intra- and intermolecular hydrogen bonding in ternary mixtures of PVP-PEGs-PPG system in dilute solutions of non-polar solvent. A comparative study has been conducted to explore the change in molecular dynamics and intra- and intermolecular interactions with the increase in molecular weight of PEGs and varying PVP concentration in the mixtures using the microwave dielectric relaxation times.

2. Experimental

Materials :

Poly(vinyl pyrrolidone) (PVP) of average molecular weight Mw = 40,000 g mol^{-1} of LR grade was obtained from Loba chemie, India. Poly(propylene glycol) (PPG) of average molecular weight 2000 g mol^{-1} of LR grade was obtained from BDH, India. The poly(ethylene glycol)s (PEGs) of different molecular weight *i.e* 200, 400 and 600 g mol^{-1} of LR grade were purchased from S.D. Fine-chem, India. Benzene of spectroscopic grade obtained from BDH, India, was used as non-polar solvent.

The binary mixtures of PEG200-PPG, PEG400-PPG and PEG600-PPG were prepared by mixing them in equal volume. The ternary mixtures were prepared by adding 5, 10, 15, and 20wt% PVP in the weight of equal volume binary mixtures of PEGs-PPG. The ternary mixtures were kept for approximately 48 hours for the complete dissolution of PVP in the prepared mixtures. It is observed that the dissolving rate significantly decreases with increase in molecular weight of PEGs. Five dilute solutions of each ternary mixture with increasing weight fraction (below 0.1 weight fraction of the mixture) were made in benzene solvent for their dielectric measurements.

Dielectric measurements :

The permittivity ε' and dielectric loss ε'' in dilute solutions of benzene at 10.1 GHz were determined using the short-circuited wave-guide method suggested by Heston *et al* [27]. The wave-guide method is the most accurate for the measurement of the values of ε' and ε'' of polar mixtures in non-polar solvent at very low concentrations. The static dielectric constant ε_0 was measured at 1 MHz using heterodyne beat method. High frequency permittivity ε_∞ was taken as the square of the refractive index n_D^2, which was measured with Abbe's refractometer at the wavelength of sodium light. All measurements were made at 35 ± 0.5°C.

3. Data analysis

It has been observed that ε_0, ε', ε'' and ε_∞ are linear functions of weight fractions of the individual, binary and ternary mixtures in benzene solvent. The linear slopes a_0, a', a'' and a_∞ corresponding to ε_0, ε', ε'' and ε_∞ *versus* weight fractions of the solute mixtures in non-polar benzene solvent are recorded in Table 1. These linear slopes are used for the determination of the average relaxation time τ_0, distribution parameter α, relaxation time corresponding to segmental motion τ_1, and group rotation τ_2. The values of τ_0 and α were evaluated by Higasi's [28] single frequency measurement equations proposed for dilute solutions in non-polar solvent.

The relaxation times corresponding to segmental motion τ_1, and group rotations τ_2 were evaluated by using the equations of Higasi *et al* [29] proposed for dilute solutions. These equations are described elsewhere [24]. The dielectric free energy of activation ΔF_τ was also determined by using the Eyring formula [30].

The calculated values of τ_0, α, τ_1, τ_2 and ΔF_τ of various ternary mixtures of PVP-PEGs-PPG in benzene solvent are reported in Table 2. Earlier [4,5,23-26] measured values of relaxation times of individual polymers and their binary mixtures has also been included in Table 2 for comparison. These comparative values are used to explore the molecular dynamics of the binary and ternary mixtures in non-polar solvent. In order to make data analysis more clear, the values of the relaxation times of these binary and ternary mixtures are plotted against PVP wt% in Figure 1.

4. Results and discussion

In general, the molecular dynamics of binary and ternary mixtures of associating molecules is predicted by comparing the values of relaxation times of the mixture and their constitutions in the

Table 1. Values of the slopes of ε_0, ε', ε'' and ε_∞ *versus* weight fractions of PEGs, PPG, binary mixtures of PEGs-PPG and PVP-PEGs and ternary mixtures of PVP-PEGs-PPG in dilute solution of benzene at 35°C

Polymer/their mixtures				$a_{-\infty}$
PPG 2000	3.68	1 18	0 64	−0 12
PEG 200	8 15	3 13	1 15	0 00
	PEG200-PPG binary mixture (A)			
Equal volume mixture	6.00	2.60	1 30	−0.10
PVP wt% in PEG	PVP-PEG200 binary mixtures			
5	7 69	3 95	2.10	−0.08
10	7.37	3.23	2.00	−0.08
20	5.81	2 46	1 41	−0 07
PVP wt% in A	PVP-PEG200-PPG ternary mixtures			
5	5.00	3.27	1.17	−0 14
10	4.31	2 20	0 83	−0 10
20	3.44	2.12	1.03	−0 08
PEG 400	5 71	3 33	1 20	−0 15
	PEG400-PPG binary mixture (B)			
Equal volume mixture	4 62	1 79	1.09	−0 05
PVP wt% in PEG	PVP-PEG400 binary mixtures			
5	5.92	2 43	1.21	−0 04
10	5.54	2 83	1.41	−0 06
20	5 32	2.58	1 20	−0 07
PVP wt% in B	PVP-PEG400-PPG ternary mixtures			
5	3.83	2.31	0.91	−0.04
10	3 18	2 17	0 85	−0 14
15	2.86	1 68	0.61	−0 10
PEG 600	5.00	3.33	1 28	−0.07
	PEG600-PPG binary mixture (C)			
Equal volume mixture	4.12	1 53	0 82	−0 12
PVP wt% in PEG	PVP-PEG600 binary mixtures			
5	6.19	2.50	1 10	−0 05
10	5.00	2.19	0.94	−0.06
20	4.38	2.31	0 96	−0.05
PVP wt% in C	PVP-PEG600-PPG ternary mixtures			
5	3.10	2 00	0.89	−0.13
10	2.72	1 89	0.71	−0.14
15	2.28	1 60	0.57	−0 09

Table 2. Microwave dielectric relaxation parameters of PEGS, PPG, PEGs-PPG, PVP-PEGs and PVP-PEGs-PPG mixtures in benzene solution at 35°C.

Polymers/their mixtures	τ_0 (ps)		τ_1 (ps)	τ_2 (ps)	ΔF_τ (kcal mol^{-1})
PPG 2000	58.3	0.55	63.2	8 0	3 64
PEG 200	52.0	0 63	70 1	6.0	3.50
	PEG200-PPG binary mixture (A)				
Equal volume mixture	23.6	0 48	42.3	7 8	3.06
PVP wt% in PEG	PVP-PEG200 binary mixtures				
5	14 4	0 37	28.1	8.2	2 77
10	20 7	0 37	32 6	9 5	2 99
20	24 2	0 46	40 3	8 1	3 09
PVP wt% in A	PVP-PEG200-PPG ternary mixtures				
5	10 0	0 45	29.4	6 2	2.54
10	8 5	0 47	29 8	5 6	2.44
20	9.3	0.30	20 2	7.4	2.49
PEG 400	8 5	0 49	31 9	5.6	2 41
	PEG400-PPG binary mixture (B)				
Equal volume mixture	29 7	0.43	42.0	9.6	3.20
PVP wt% in PEG	PVP-PEG400 binary mixtures				
5	28 3	0 50	45 4	7 7	3 18
10	14 4	0.41	30 3	7 7	2.77
20	16 6	0 47	35 9	7.1	2 86
PVP wt% in B	PVP-PEG400-PPG ternary mixtures				
5	8 6	0 42	26 3	6 1	2 44
10	6 2	0.33	18 7	5 8	2.25
15	8 0	0 49	30 5	5 4	2.40
PEG 600	7 0	0 35	20 9	6.1	2 29
	PEG600-PPG binary mixture (C)				
Equal volume mixture	35 8	0.51	51 1	8 0	3 31
PVP wt% in PEG	PVP-PEG600 binary mixtures				
5	32.9	0 56	52 9	6.8	3.28
10	24 1	0 54	47 1	6.6	3 08
20	12 7	0 48	34.0	6.4	2.69
PVP wt% in C	PVP-PEG600-PPG ternary mixtures				
5	7.7	0.32	19 5	6.6	2.38
10	5 7	0.34	18 4	5.5	2.19
15	5 4	0.35	18 8	5.3	2.15

same environment. Therefore, before the interpretation of PVP-PEGs-PPG ternary mixture dynamics, it is indispensable to report here the characterization of molecular dynamics of the molecules of PEGs, PPG and binary mixtures of PEGs-PPG and PVP-PEGs, explored earlier in this laboratory using microwave dielectric relaxations in benzene solvent.

(i) Molecular dynamics of PEGs :

A systematic microwave dielectric relaxation study [4,5] of homologous series of poly (ethylene glycol)s, average molecular weight ranging from 200 to 9000 g mol^{-1} in dilute solutions of benzene at 9.83 GHz confirmed that there is large tendency towards the increase in coiling of the molecular chain of these molecules with the increase in degree of polymerization. The increase in chain coiling with increase in molecular weight is also supported by decrease in specific dipole moment [5] with increase in the degree of polymerization. The extent of intermolecular hydrogen bonding decreases with the increase in chain length of PEG molecules. Further, the chain ends hydroxyl groups of these molecules are in dynamic equilibrium

with the formation of five membered intra-molecular hydrogen bonded rings.

(ii) Molecular dynamics of PPG2000 :

Microwave dielectric relaxation study [23] of PPG2000 in benzene, carbon tetrachloride, cyclohexane and decaline solvent confirmed that besides the presence of side methyl groups in

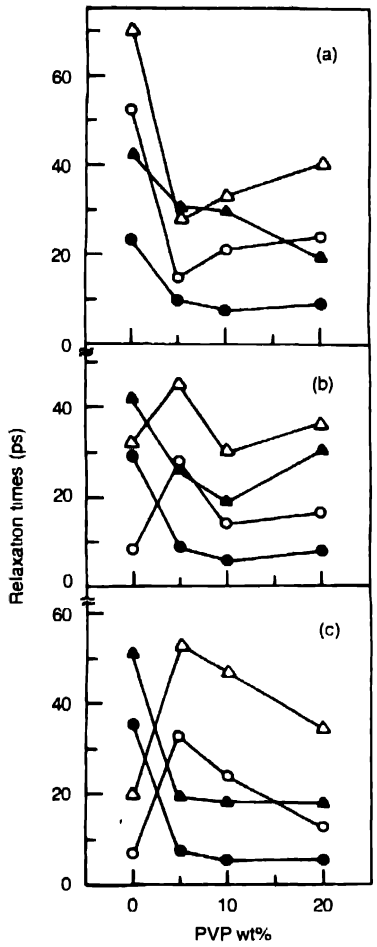

Figure 1. Plots of relaxation times *versus* PVP wt%.
(a) PVP-PEG 200 and PVP-PPG-PEG 200 mixtures
(b) PVP-PEG 400 and PVP-PPG-PEG 400 mixtures
(c) PVP-PEG 600 and PVP-PPG-PEG 600 mixtures
τ_0 : binary mixtures (o) ; ternary mixtures (•)
τ_1 : binary mixtures (Δ) , ternary mixtures (▲)

the repeating units, there is also coiling in PPG molecular chain, and the hydrogen bonded network of these molecules has transient structure in non-polar solvent. Further, Kirkwood correlation factor proved that in PPG molecules, hydrogen bonding is weak in comparison to the hydrogen bonding of PEG molecules [31-34]. The presence of side groups in the molecular chain of polymers reduces chain flexibility and increases hindrance to the reorientation of the molecules as a whole, in comparison to the polymer chain without side-groups, which is confirmed by dielectric and other relaxation studies [35]. In case of PPG molecules, segmental motion is also found highly hindered due to presence of methyl side groups and there is rotation of methyl side groups with the ends hydroxyl groups in dynamic equilibrium.

(iii) Molecular dynamics in PPG-PEGs mixtures :

The molecular dynamics [24] of the equal volume binary mixtures of PPG-PEGs changes significantly due to heterogeneous molecular interactions, chain coiling and elongation of the network in dilute solutions in comparison to the molecular dynamics of the individual molecules. In these mixtures due to heterogeneous interactions, H-bonded homogeneous and heterogeneous cooperative domains are formed during their mixing. The elongation of the cooperative domains in dilute solutions is found influenced by the chain length of PEG molecules. Further, from the τ_2 values of the binary mixtures, it was concluded that the intra-molecular groups' rotations has very local character in binary mixtures of PPG-PEGs with increase in PEG chain length. This fact is also confirmed by other studies [36-38].

(iv) Molecular dynamics in PVP-PEGs mixtures :

In PVP-PEGs mixtures, the molecular dynamics is governed by the value of number of hydroxyl groups of PEG molecules in comparison to the value of number of carbonyl groups of the PVP molecules and also the flexibility of the molecular chain of PEG molecules those bridges the long coiled PVP chain through hydrogen bonding. Due to complex formation between PVP and PEG molecules, flexible and dynamic supermolecular heterogeneous network is formed as discussed earlier [9,26] The high degree complex formation in PVP-PEG200 mixtures produces more hindrance to molecular reorientation and segmental motion in comparison to the hindrance of molecular reorientation in PVP-PEG400 and PVP-PEG600 mixture [26] Further, the molecular dynamics in these mixtures in non-polar benzene solvent, also vary with the increase in PVP concentration. It is confirmed that the molecular dynamics of these binary mixtures is independent of the mixture viscosity Using FTIR measurements, Feldstein *et al* [9] confirmed that in PVP-PEG mixtures, all hydroxyl groups not form the complexes with the carbonyl groups, and hence homogeneous clusters of PEGs are also exists in the mixtures in dilute solutions. In dilute solutions of non-polar solvent, besides the segmental motion and intramolecular groups rotations, there is rotations of PEG molecules as a whole in PVP-PEGs mixtures.

(v) Molecular dynamics in PVP-PEGs-PPG mixtures :

Average relaxation time (τ_0) :

The value of τ_0 depends on the hindrance offered by the intermolecular interactions and molecular chain coiling. In binary and ternary mixtures heterogeneous interactions significantly alter the relaxation times. The τ_0 value of PVP-PEG200-PPG

mixtures is found small in comparison to the τ_0 values of PPG, PEG200, equal volume binary mixtures of PPG-PEG200, and different concentration binary mixtures of PVP-PEG200 in benzene solutions at 35°C (Table 2). Further in this ternary mixture, the τ_0 values are found almost independent of the PVP concentration (Figure 1a). These observed values suggest that in ternary mixture due to breaking of homogeneous network, a cooperative heterogeneous system in dynamic equilibrium is formed, which favours the molecular dynamics, and hence the τ_0 value decreases for ternary mixture in comparison to the τ_0 values of individual constituent polymers and their binary mixtures. In case of PVP-PEG200 binary mixtures, the increase in τ_0 value with the increase in PVP concentration is due to the elongation of the PVP-PEG200 network in benzene solution [26]

In case of PVP-PEG400-PPG mixtures, the observed τ_0 values are smaller than the corresponding τ_0 values of PPG, PEG400-PPG and PVP-PEG400 binary mixtures with PVP concentration variation, but these are equal to the τ_0 value of PEG400 in benzene solution (Figure 1b). From the equal τ_0 values of ternary mixtures and PEG 400, it seems that in the ternary mixture, there is also larger probability of the reorientation of PEG400 molecules in the complex network due to the breaking and reforming of hydrogen bond in dynamic equilibrium of the heterogeneous network.

Similarly in case of PVP-PEG600-PPG ternary mixtures, the evaluated τ_0 values are also found lower than those of PPG, PEG600, PPG-PEG600 and PVP-PEG600 (Figure 1c). But these τ_0 values are nearly equal to the values of PEG600 molecules. This also suggests that in this mixture, there is larger possibility of the reorientation of PEG600 molecules in the heterogeneous polymer network in dilute solutions of benzene. Further, the small τ_0 values in these ternary mixtures, show that there is elongation of the heterogeneous network in dilute solutions of benzene. As confirmed by Feldstein *et al* [18], all PEG ends -OH groups not form complexes with the carbonyl groups of the monomer units of PVP chain. Due to this, there are large number of unassociated PEG molecules in the heterogeneous network and these unassociated PEG molecules reorient as a whole, in the elongated network in dilute solution of the benzene when subjected to the microwave frequency electric field.

In all these ternary mixtures studied, the evaluated values of distribution parameter α are large ($\approx$ 0.30 to 0.50). Earlier, Shukla *et al* [39] studied the poly (ethyl methacrylate) (PEMA) and poly (n-butyl isobutyl methacrylate) (PBiBMA) in dilute solutions of benzene at 10 GHz and found the values of α in the range of 0.53 – 0.57. The large values of α of these polymers and their mixtures show that besides the overall rotation of the molecules, there is larger probability of the segmental motion and group rotations to the relaxation processes.

Relaxation time corresponding to segmental motion (τ_1) :

The τ_1 values of these individual polymers and their binary and ternary mixtures are found higher than the corresponding τ_0 values. This shows that the segmental motion in these associated polymers and their mixtures are influenced by the flexibility in the polymer chain and also by the hindrance due to presence of the side-groups in the chain. Table 2 shows that in the ternary mixtures, there is anomalous variation in the τ_1 values of PVP-PEG200-PPG and PVP-PEG400-PPG with the increase in concentration of PVPin the equal volume PEG-PPG binary mixtures. But the τ_1 values of PVP-PEG600-PPG are found independent of the PVP concentration (Figure 1). This anomalous variation in τ_1 values shows that the distribution of relaxation times is governed by the strength of intra- and inter-molecular interactions in the complex network formed between the mixed polymers in dilute solutions. With increasing concentration of PVP in binary and ternary mixtures, there is large increase in the viscosity of the system but the observed anomalous values of relaxation times confirm that the molecular segmental motion is independent of the mixture viscosity and strongly depends on the molecular association and rigidity in the polymer chain. Earlier[40], it was also confirmed that the relaxation times of PVP-PEG mixtures are independent of their viscosity.

Relaxation time for group rotation (τ_2) :

The observed τ_2 values of these polymers and their binary and ternary mixtures vary in the range $\simeq$ 5.0 to 10 ps (Table 2). In case of PEG molecules [4], the τ_2 values are assigned to the rotation of chain ends hydroxyl groups while in case of PPG molecules [23] besides the rotation of their molecular chain ends hydroxyl groups, there is also the rotation of methyl side-groups of the PPG chain. In binary mixtures of PEGs-PPG molecules [24], there is also the rotations of –OH groups and the methyl side-groups, but results show that the variation in τ_2 values of the binary mixtures is small in comparison to those of individual molecules which confirmed that the group rotations is in dynamic equilibrium. In case of PVP-PEG mixtures, it is found that there is slight decrease in τ_2 values with increase in PEGs chain length. Due to increase in PEGs chain length, there may be decrease in the strength of the hydrogen bonding and hence τ_2 decreases. But in case of PVP-PEGs-PPG ternary mixtures, the τ_2 values vary in the range of 5.3–7.4 ps with the variation in PVP concentration and increase with PEGs chain length. This small variation in τ_2 values show that in ternary mixtures, after intra- and intermolecular hydrogen bonding, the nature of the rotating polar groups remains same.

The free energy of activation ΔF_τ of these polymers and their binary and ternary mixture were also evaluated using the average dielectric relaxation time τ_0 and found in the range

2.15–3.64 kcal mol^{-1}, which is corresponding to the breaking of hydrogen bonds in dilute solutions. These values of activation energies also confirm that the molecular networks of ternary mixtures are highly flexible and the molecular dynamics is in dynamic equilibrium in dilute solutions of non-polar solvent.

5. Conclusion

The comparative dielectric relaxation studies of these challenging associating systems confirmed that the molecular dynamics in ternary mixtures is governed by the intra- and intermolecular interactions and the molecular chain coiling and flexibility. But these molecular motions are independent of the viscosity of the mixture. The observed values of τ_0 confirmed that in these ternary mixtures, there is large probability of the reorientation of the PEG molecules as a whole in the hydrogen-bonded polymeric heterogeneous network. From the dielectric relaxation studies, it is inferred that the ternary mixture matrix of PVP-PEGs-PPG is suitable for the TDDS of drugs of the molecular size equal to PEGs molecules *i.e.* 200-600 because of the reorientation of the PEGs molecules in the heterogeneous network.

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